



Capsule Report

Aqueous Mercury Treatment



Capsule Report:
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National Risk Management Research Laboratory
Office of Research and Development
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James Patterson, of Patterson and Associates, Inc., Chicago, IL was the primary author.

Technical reviewers of this report were:

Richard Osantowski, Radian international Corporation, Milwaukee, WI
Thomas Sorg, National Risk Management Research Laboratory, USEPA, Cincinnati, OH
Donald Sanning, National Risk Management Research Laboratory, USEPA, Cincinnati, OH
Jerry Stober, Environmental Services Division, USEPA, Athens, GA

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Chapter 1

Executive Summary

1.1 Purpose

This report describes established technologies and identifies evolving methods for treating aqueous mercury. The information provided encompasses full-, pilot- and bench-scale treatment results as presented in the technical literature. The report describes alternative technologies in terms of (1) governing physical and chemical principles (e.g., solubility, oxidation-reduction potential, volatility), (2) key treatment parameters (e.g., speciation, pH, precipitating agent type and dosage, or adsorbent type and dosage), (3) pretreatment requirements, treatment performance, advantages and disadvantages, design considerations, and economics when available. This information can be useful for evaluating mercury treatment alternatives for industrial wastewater, groundwater, and soil washing extract.

This document assumes that the reader is already well versed with the technologies described and is using this report to better understand each technology's applicability for aqueous mercury removal. Thus, the report does not provide basic descriptions of each technology; such information can be found elsewhere in the literature. In addition, the report does not present recommended values for the common design parameters of technologies. Values for such parameters as (1) contact time, (2) volumetric loading rates, (3) dosages, (4) reaction times, (5) breakthrough times, and (6) mixing requirements can be determined by conducting treatability studies using the wastewater to be treated.

1.2 Summary

A broad spectrum of mercury treatment technologies has been described in the technical literature, ranging from established full-scale applications to innovative approaches

investigated to date only at bench or pilotscale. The literature, however, provides only limited information on actual full-scale treatment technology performance and almost no full-scale economic data or information on mercury recovery.

Well-established and widely reported full-scale technologies are precipitation, coagulation/co-precipitation, and activated carbon adsorption. Representative data from aqueous mercury treatment operations using these methods are provided in this report.

Another technology is ion exchange treatment, which has historically been limited to the use of anion resins to process industrial wastewater that contains inorganic mercury in the complex mercuric chloride form. Chapter 8 provides a case study illustrating the use of an ion exchange system for mercury removal.

Other, less-established methods for treating aqueous mercury that are discussed in this report include chemical reduction, membrane separation, and emerging technologies involving macrocycles adsorption, biological treatment, and membrane extraction.

Each of the mercury treatment technologies described in this report achieves different effluent mercury concentrations. The effectiveness of treatment provided by each type of technology depends on the chemical nature and initial concentration of mercury as well as the presence of other constituents in the wastewater that may interfere with the process. As indicated by example data provided, co-precipitation and ion exchange achieve the lowest effluent mercury concentrations for many waste streams, ranging from 0.5 to 5.0 $\mu\text{g/L}$. Membrane technology typically achieves 80 to 90 percent rejection of mercury. Other factors, however, such as residuals management and costs, weigh heavily in selecting the appropriate treatment approach.

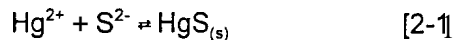
Chapter 2

Precipitation Treatment Process

This chapter presents information on precipitation and coagulation/co-precipitation technologies, which are among the most well-established approaches for removing mercury from wastewater. The information provided includes example data from aqueous mercury treatment operations using these methods.

2.1 Sulfide Precipitation

One of the more commonly reported precipitation methods for removal of inorganic mercury from wastewater is sulfide precipitation. In this process, sulfide (e.g., as sodium sulfide or another sulfide salt) is added to the wastestream to convert the soluble mercury to the relatively insoluble mercury sulfide form:



As with other precipitation treatment, the process is usually combined with pH adjustment and flocculation, followed by solids separation (e.g., gravity settling, filtra-

tion). A typical process flow diagram for sulfide precipitation is shown in Figure 2-1. The sulfide precipitant is added to the wastewater in a stirred reaction vessel, where the soluble mercury is precipitated as mercury sulfide. The precipitated solids can then be removed by gravity settling in a clarifier as shown in Figure 2-1. Flocculation, with or without a chemical coagulant or settling aid, can be used to enhance the removal of precipitated solids.

Table 2-1 presents example sulfide treatment results. For initial mercury levels in excess of 10 mg/L, sulfide precipitation can achieve 99.9+% removal. Even with polishing treatment such as filtration the minimum effluent mercury achievable appears to be approximately 10 to 100 $\mu\text{g/L}$. The most effective precipitation, with regard to minimizing sulfide dosage, is reported to occur in the near-neutral pH range. Precipitation efficiency declines significantly at pH above 9 (Patterson, 1985). Sulfide precipitation appears to be the common practice for mercury control in many chlor-alkali plants. removal efficiencies of 95 to 99.9 percent are reported for well designed and managed

Figure 2-1 Sulfide precipitation.

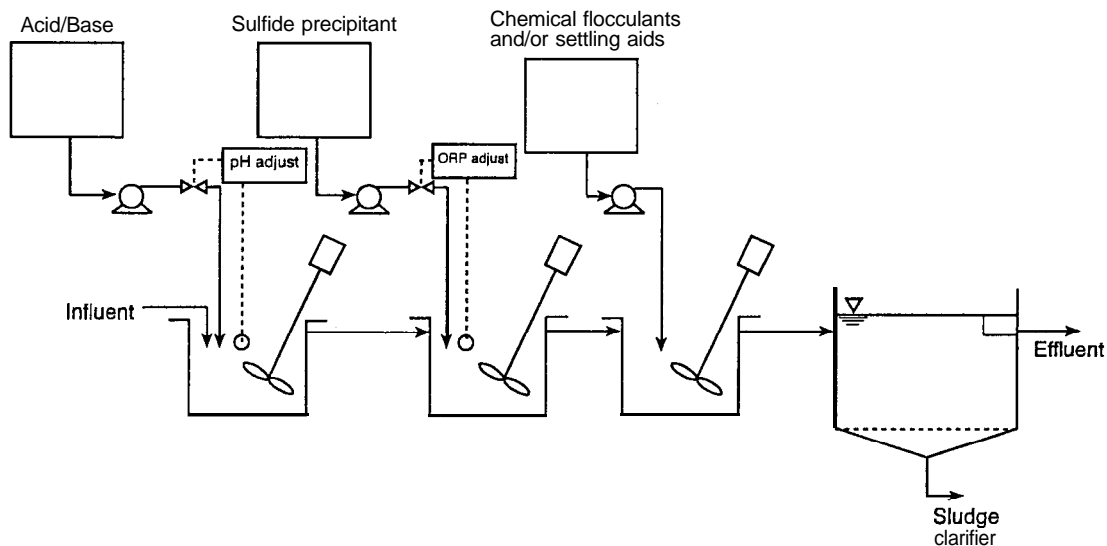


Table 2-1. Sulfide Precipitation Treatment for Mercury (After Patterson, 1985)

Treatment Chemical	Mercury Concentration ($\mu\text{g/L}$)		Percent Mercury Removal	Treatment pH	Additional Treatment
	Initial	Final			
Sodium sulfide	NA	<3	NA	NA	Vacuum filter
	300-6,000	10-125	58-99.8	NA	Pressure filter
	1,000-50,000	10	99-99.9	NA	Flocculation + activated carbon
Sodium hydrosulfide	131,50	20	>99.9	3.0	"Filter"
Magnesium sulfide	5,000-10,000	10-50	99-99.9	10-11	None
"Sulfide" salt	300-6,000	10-125	58-99.8	5.1-8.2	Filtration
		(50 avg)			
	NA	100-300	NA	NA	None
	NA	100	NA	NA	None
	NA	10-20	NA	NA	Activated carbon

NA = Not available.

treatment Mercury systems (Perry, 1974; U.S. EPA, 1974). A mercury effluent level of about $65 \mu\text{g/L}$ has been reported for sodium sulfide treatment of wastewaters from the chlor-alkali industry; influent mercury concentration was not reported (U.S. EPA, 1974). Costs of using the sulfide process for the treatment of chlor-alkali wastewater were reported to be \$0.79/1,000 gal (1987 basis), exclusive of sludge management. Capital cost (adjusted to 1995 basis) for a chlor-alkali plant utilizing sodium sulfide addition plus diatomaceous earth filtration for a 100-gpm flow was \$2,767.47 /1,000 gpd capacity (Perry, 1974). One consequence of the application of sulfide precipitation technology is stockpiles of mercury-laden process sludges, which must be either disposed of in an environmentally acceptable manner or processed for mercury recovery. Thus, the sludge management approach chosen is a key factor in evaluating the sulfide process for treating such wastewater.

In addition to its inability to reduce mercury below 10 to $100 \mu\text{g/L}$, other drawbacks of this method include: (1) the formation of soluble mercury sulfide species at excess dosage of sulfide, due to the common ion effect, (2) the difficulty of real-time monitoring of reactor sulfide levels, (3) the generation of toxic residual sulfide in the treated effluent (a potential problem), (4) the difficulty of clarification and sludge processing, and (5) the need to dispose of sulfide sludges. Investigators have reported that mercury can resolubilize from sulfide sludges under conditions that can exist in landfills (Hansen and Stevens, 1992). This could in mercury contamination of leachate and potential result ground-water pollution.

2.2 Coagulation/co-precipitation

Information is available in the literature on the removal of both inorganic and organic mercury by coagulation/co-precipitation for a variety of mercury-containing wastewaters (Patterson, 1985). Coagulants employed include aluminum sulfate (alum), iron salts, and lime. For alum and iron, the dominant mercury removal mechanism is most likely by adsorptive co-precipitation (Patterson et al., 1992). Here, one ion is adsorbed into another bulk solid, formed, for example, by addition of alum and precipitation of aluminum hydroxide or by addition of an iron (ferrous or ferric) salt and precipitation of iron hydroxide. The adsorption process is isothermal, and treatment performance can be enhanced by optimal bulk solids formation and by pH manipulation to optimize bulk solid surface change and soluble mercury speciation.

In studies on the treatment of inorganic mercury dosed to domestic sewage, both iron and alum co-precipitation, followed by filtration, reduced initial mercury levels of 50 to $60 \mu\text{g/L}$ by 94% to 98%. Lime coagulation treatment, applied at a higher mercury level of $500 \mu\text{g/L}$, achieved 70 percent removal upon filtration (Patterson, 1985). Treatment data for coagulation/co-precipitation are summarized in Table 2-2. Effluent levels of mercury achieved by alum treatment range from 1.5 to $102 \mu\text{g/L}$, with a typical 5 to $10 \mu\text{g/L}$ value, and by iron treatment from 0.5 to $12.8 \mu\text{g/L}$.

Table 2-2. Coagulation/co-precipitation Treatment Results for Mercury (After Patterson, 1985)

Coagulant Salt	Coagulant Dosage (mg/L)	Mercury, $\mu\text{g/L}$		Percent Mercury Removal	Treatment pH	Additional Treatment
		Initial	Final			
Alum	1,000	11,300	102	99	3	Filtration
	100	90	11	88	NA	—
	100	NA*	10	NA	NA	—
	21-24	5.9-8.0	5.3-7.4	10-34	6.7-7.2	Filtration
	NA	50	26.5	47	7.0	Filtration
	220	60	3.6	94	6.4	Filtration
	20-30	3-8	1.5-6.4	50-81	NA	—
	20-30	3-16"	2.3-21.3	<23	NA	—
Iron	34-72	4.0-5.0	2.5	38-50	6.9-7.4	Filtration
	NA	50	3.5	93	8.0	Filtration
	40	50	1.0	98	6.2	Filtration
	20-30	1-17	0.5-6.8	50-97	NA	—
	20-30	2-17'	1.2-12.8	40-93	NA	—
Lime	415	500	150	70	11.5	Filtration
	NA	0.66	0.2	>69	8.3	—

*Organic mercury.
 NA = Not available.
 - = None

Chapter 3

Adsorption Processes

Adsorption processes have the potential to achieve high efficiencies of mercury removal and/or low effluent mercury levels. The predominant adsorption process utilizes activated carbon, but the use of other adsorbents also are reported in the literature. These include processed vegetable or mineral materials such as bicarbonate-treated peanut hull carbon (BPHC), modified *Hardwickia binata* bark (MHBB), coal fly ash, and the Forager sponge (Namasivayam and Periasamy, 1993; Sen and De, 1987; Deshkar et al., 1990; U.S. EPA, 1994b). Metal hydroxides are also used as adsorbents. When metal hydroxides are employed for adsorptive treatment, the process is commonly termed coagulation or co-precipitation. (This process is discussed in Chapter 2.) An inherent advantage of adsorptive treatment, particularly when the adsorbent displays isothermal or quasi-isothermal behavior, is that increased treatment efficiency results

from incremental adsorbent dosage. Isothermal behavior is observed when, for a fixed initial pollutant concentration, decreasing residual soluble concentrations are observed as the dosage of adsorbing treatment material is added. Unless adsorbent recovery is feasible, these incremental dosages also result in production of increased wastewater treatment residuals, requiring ultimate disposal. Variables other than adsorbent type and dosage can also affect adsorption efficiency. Common variables include wastewater pH and pollutant speciation.

4.1 Activated Carbon Adsorption

Granular activated carbon (GAC) is the most commonly used adsorbent system for treating industrial waste (U.S. DOE, 1994). This process is used in a variety of configurations, as demonstrated in Figures 3-1 and 3-2. GAC systems may be either pressure or gravity type. They may

Figure 3-1. Types of GAC column design (Calgon Carbon Corp.)

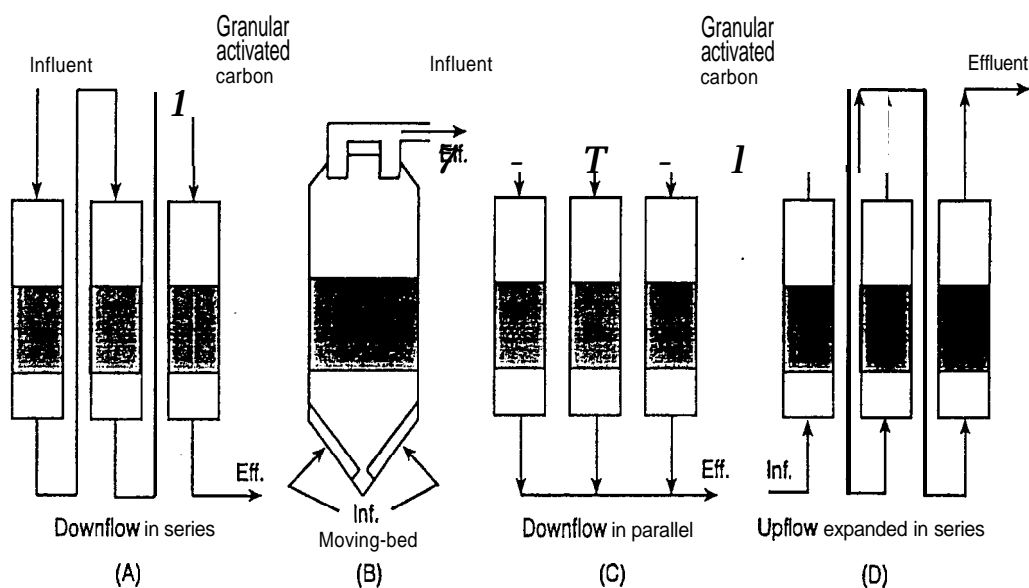
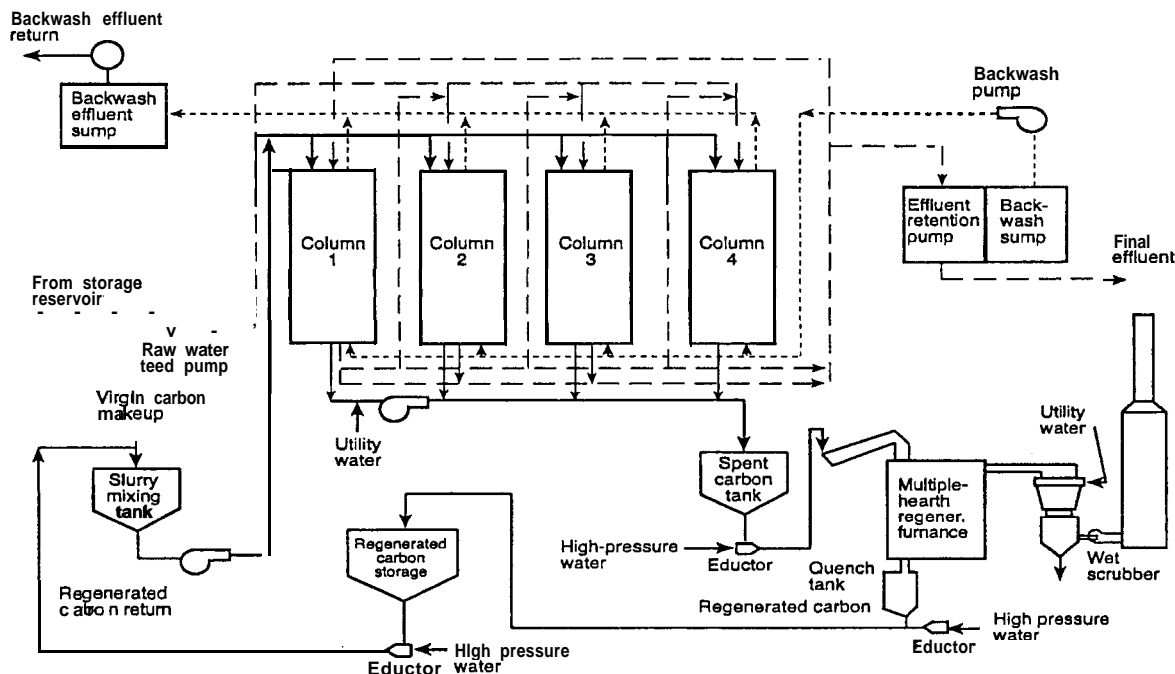


Figure 3-2. GAC process flowsheet (after Eckenfelder, 1989)



be upflow counter-current type with packed or expanded carbon beds, or upflow or downflow fixed-bed units with multiple columns in series (Figure 3-1). Contaminated water is passed through the columns until the key contaminant is detected at a predetermined level in the effluent. When multiple columns are placed in series, the first column can be loaded to a greater capacity, while residual levels of the contaminant are removed in the downstream columns. When a column has been loaded to its design capacity, it may be regenerated or the spent carbon can be replaced while another column is brought online. An alternative method of carbon treatment involves use of powdered activated carbon (PAC). The PAC is typically added as a slurry into a contact reactor, and the PAC solids subsequently are removed in a solids separation stage. The PAC is normally not regenerated for reuse due to unfavorable economics including poor recovery of the PAC.

Table 3-1 summarizes example activated carbon mercury treatment data. The removal of mercury from potable water using PAC was studied by Thiem and colleagues (1976). Treating a spiked water solution containing 10 $\mu\text{g/L}$ total mercury, they achieved approximately 80% removal at a pH of 7 and a PAC dosage of 100 mg/L. The study also demonstrated that the addition of mercury chelating agents, such as ethylene diamine triacetic acid (EDTA) or tannic acid, prior to contact with the PAC increased mercury removal efficiency. Concentrations as low as 0.02 mg/L EDTA and 1 mg/L tannic acid increased mercury removal efficiencies by 10% to 20%.

The mercury removal efficiencies by concentrations of 50 to 200 mg/L also increased mercury removal efficiencies by 10% to 20% over those obtained by PAC alone.

The removal of mercury (II) from synthetic wastes by 11 different brands of commercial activated carbon was studied by Huang and Blankenship (1984). Among the 11 different types of activated carbon, Nuchar SA and Nuchar SN exhibited a high percent (>99.9) mercury (II) removal over a wide pH range (2.5 to 11). The other activated carbons studied displayed maximum total mercury (II) removal at pH 4 to 5, and the percent mercury (II) removal dropped markedly at pH values greater than and less than 4 to 5.

Pretreatment or modification of activated carbon with carbon disulfide solution before use, has been shown to enhance mercury removal. Humenick and co-investigators (1974) utilized an activated carbon that was presoaked in carbon disulfide and then dried and used as PAC. The pretreated activated carbon removed mercury from an initial concentration of 10 mg/L down to 0.2 $\mu\text{g/L}$, versus the 4 mg/L effluent value obtained with the untreated carbon. The enhanced mercury removal was attributed to chemisorption reactions. Sulfur atoms have a high affinity for mercury, as evidenced by the K_{sp} of HgS (see Table 2-2). The mercury removal mechanism proposed by Humenick and colleagues (1974) involves transport and diffusion to the carbon disulfide sites and subsequent formation of a chemical bond between a carbon disulfide molecule and the mercury ion.

Table 3-1. Activated carbon mercury treatment results

Activated Carbon Type	Mercury Concentration ($\mu\text{g/L}$)		Percent Removal	Additional Treatment	Other Conditions	Reference
	initial	Final				
PAC	10,000	4,000	60	None	SW, BS	Humenick et al., 1974
PAC	10,000	0.2	>99.9	5 μm filtration, PAC presoaked in CS_2 and dried	SW, BS	Humenick et al., 1974
PAC	2,000	NA	-100	Centrifugation or 0.45 μm filtration	SW, BS	Huang and Blankenship, 1984
PAC	10	NA	-80	0.45 μm filtration	SW, BS	Thiem et al., 1976
PAC	1.0	0.5	50	Settling	PW, BS	Guarino et al., 1988
GAC	0-100	<1.0	>41	None	SF, FS	E.C. Jordan Co., 1989
GAC	1.7 1.5	0.9 0.8	47 47	Filtration	PW, BS	Guarino et al., 1988

PAC = Powdered activated carbon.
 GAC = Granular activated carbon.
 BS = Bench scale.
 SW = Synthetic wastewater.
 PW = Petrochemical wastewater.
 SF = Superfund wastewater.
 FS = Full scale.
 NA = Not available.

A study was conducted by Guarino and co-investigators (1988) to establish the feasibility of using activated carbon as an advanced treatment method for petrochemical wastewater. This study investigated petrochemical wastewater at bench scale, utilizing GAC and PAC. Low initial mercury levels of 1.5 and 1.7 $\mu\text{g/L}$ were reduced to 0.8 and 0.9 $\mu\text{g/L}$, respectively, using GAC, while an initial mercury concentration of 1.0 $\mu\text{g/L}$ was reduced to 0.5 $\mu\text{g/L}$ using PAC. The performance data reported in the literature suggests that activated carbon treatment can achieve a residual mercury level of 0.5 to 20 $\mu\text{g/L}$, dependent in part on the initial wastewater mercury level (Patterson et al.).

Gates and colleagues (1995) conducted laboratory work to investigate the feasibility of using inexpensive sulfur-impregnated activated carbon beads, known as Mersorb, for mercury removal from aqueous waste. These studies were conducted to evaluate the treatability of mercury-containing aqueous and solid mixed wastes stored at DOE sites, such as the Oak Ridge Y-12 site. The from aqueous solutions to below 0.2 mg/L. Mersorb worked

under acidic conditions (pH of 2), but its capacity at low pH was reduced by 50% compared with neutral conditions. Mersorb beads reportedly had favorable process economics compared with ion exchange.

3.2 Xanthate Treatment

An alternative adsorption material to activated carbon is starch xanthate, yielding mercury-starch xanthate. One modification is termed the Metals Extraction by Xanthate Insolubilization and Chemical Oxidation (MEXICO) process, also termed the Advanced MEXICO Precipitation Process (Macchi et al., 1985; Tiravanti et al., 1987). Most published data on this process appears to be from bench- and pilot-scale studies. No published information was available on full-scale application.

Example data for starch xanthate treatment are presented in Table 3-2. Campanella and colleagues (1986) were able to reduce the mercury concentration in a synthetic wastewater at bench scale from 10 to 23 $\mu\text{g/L}$

Table 3-2. Starch Xanthate Treatment for Mercury

Mercury Concentration (mg/L)		Treatment pH	Additional Treatment	Other Conditions	Reference
Initial	Final				
10	0.023	1	Sedimentation	SW, BS	Campanella et al., 1986
100	0.001	5	0.45 μm filtration	SW, BS	Tiravanti et al., 1987
9.5	0.01-0.1	5	Sedimentation	cw, PS	Tiravanti et al., 1987
9.5	0.005-0.02	5	Sedimentation plus 0.45 μm filtration	cw, PS	Tiravanti et al., 1987
6.3	-0.2	11	10 μm filtration	cw, BS	Macchi et al., 1985
6.3	0.01	11	Sodium hypochlorite addition	CW, BS	Macchi et al., 1985
6.3	0.001	NA	Activated carbon	CW, BS	Macchi et al., 1985

SW = Synthetic wastewater.
 BS = Bench scale.
 cw = Chlor-alkali wastewater.
 PS = Pilot scale.

following sedimentation. Tiravanti and co-investigators (1987) were able to reduce mercury at bench scale from 100 to 1 $\mu\text{g/L}$ following 0.45 μm filtration. These researchers also conducted pilot-scale (15 m^3/d) experiments on chlor-alkali wastewater and were able to reduce the mercury concentration from 9.5 mg/L to a range of 10 to 100 $\mu\text{g/L}$ following sedimentation, and to a range of 5 to 20 $\mu\text{g/L}$ following sedimentation and 0.45 μm laboratory filtration (to estimate residual soluble mercury). Macchi and colleagues (1985) conducted bench-scale experiments on chlor-alkali wastewater and were able to reduce the mercury concentration from 6.3 to 200 $\mu\text{g/L}$ following 10 μm filtration, to 10 $\mu\text{g/L}$ following sodium hypochlorite addition, and to 1 $\mu\text{g/L}$ following activated carbon treatment. The process appears able to achieve an effluent mercury level of 5 to 20 $\mu\text{g/L}$.

Macchi and colleagues (1985) also reported that mercury can be recovered from the mercury-xanthate sludges by treating the precipitate with 5 M hydrochloric acid and sodium hypochlorite. The cost of sodium hypochlorite is relatively insignificant for the chlor-alkali industry, and the redissolved mercury reportedly could be recycled to the head of the chlor-alkali plant.

3.3 Other Adsorption Processes

Various other adsorbent alternatives to activated carbon have been reported to perform in comparable fashion for mercury treatment. These adsorbents include BPHC, MHBB, coal fly ash, and the Forager sponge. Each of these adsorbents is described in the following sections.

Table 4-3 presents mercury adsorption Freundlich parameter values for these adsorbents, except the Forager sponge. The Freundlich adsorption equation is:

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log C_e \quad [3-1]$$

Where:

x = the amount of solute (mercury) adsorbed
 m = the amount of adsorbent required to adsorb x
 k and $\frac{1}{n}$ = empirical constants (Freundlich parameters)

C_e = equilibrium concentration (mercury) The Freundlich parameters k and $\frac{1}{n}$ are equal to the intercept and slope

of the line obtained by plotting $\log \frac{x}{m}$ vs. $\log C_e$.

Table 3-3. Freundlich Isotherm Parameters for Mercury Adsorption

Adsorbent	k	$\frac{1}{n}$	Reference
GAC	4.68	3.16	Namasivayam and Periasamy, 1993
BPHC	42.17	3.50	Namasivayam and Periasamy, 1993
Coal fly ash (pH 2.2)	1.014	0.053	Sen and De, 1987
Coal fly ash (pH 3.1)	1.094	0.333	Sen and De, 1987
Coal fly ash (pH 4.2)	1.230	0.361	Sen and De, 1987
MHBB	1.07	0.324	Deshkar et al., 1990

GAC = Granular activated carbon.

BPHC = Bicarbonate-treated peanut hull carbon.

MHBB = Modified *Hardwickia binata* bark.

The value of k is roughly an indicator of sorption capacity, and $\frac{1}{n}$ is an indicator of sorption intensity.

3.3.1 BPHC Adsorption

From bench-scale study, using a stock mercury solution feed of 10 to 20 mg/L, Namasivayam and Periasamy (1993) reported BPHC to be seven times more effective than GAC for mercury (II) removal. This result was attributed to the higher porosity plus moderate ion exchange capacity of BPHC as compared to GAC. The Freundlich parameters shown in Table 3-3 quantify the sorption capabilities of BPHC. The desorption capabilities of BPHC also were reported to be promising. Percent recoveries of mercury from BPHC and GAC using 0.6 M HCl were 47% and 13%, respectively, and 87% and 24%, respectively, using 1.0% KI (potassium iodide). No full-scale data were available on this material.

3.3.2 MHBB Adsorption

A modified *Hardwickia Binata* bark was studied at bench-scale for its adsorption of mercury (II) from water (Deshkar et al., 1990). Although the media was shown to be effective in removing mercury (II) from water, it is not as effective as GAC, as indicated by the Freundlich parameters listed in Table 3-3. No information was reported on the desorptive properties of the *Hardwickia binafa* bark.

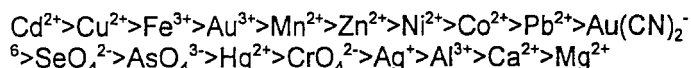
3.3.3 Coal Fly Ash Adsorption

Coal fly ash, an industrial waste solid, was shown to adsorb mercury (II) (Sen and De, 1987). Coal fly ash did not perform as well as GAC, however, as shown by the Freundlich parameters listed in Table 3-3. Maximum

mercury adsorption by coal fly ash was observed in the pH range 3.5 to 4.5 (Sen and De, 1987).

3.3.4 Forager Sponge Adsorption

The Forager sponge is an open-celled cellulose sponge with an amine-containing polymer that reportedly has a selective affinity for aqueous heavy metals in both cationic and anionic states. The polymer is reported to form complexes with ions of transition-group heavy metals, providing ligand sites that surround the metal and form a coordination complex. The polymers order of affinity for metals is reportedly influenced by solution parameters such as pH, temperature, and total ionic content. Mercury is one of the metals that is claimed to be removed by the sponge. In general, the following affinity sequence for representative ions is expected (U.S. EPA, 1994b):



The sponge can be used in columns, fishnet-type enclosures, or rotating drums. When used in a column, flow rates of 3 bed volumes per minute are reported to be obtained at hydrostatic pressure only 2 feet above the bed and without additional pressurization. Therefore, sponge-packed columns are claimed to be suitable for unattended field use.

Adsorbed ions can be eluted from the sponge using techniques typically employed to regenerate ion exchange resins and activated carbons. Following elution, the sponge can be reused in the next adsorption cycle. The number of useful cycles is reported to depend on the nature of the adsorbed ions and the elution technique

used. Alternatively, the metal-saturated sponge could be incinerated. Metals volatilization would be of concern. The

sponge may be dried and reduced in volume to facilitate disposal (U.S. EPA, 1994b).

Chapter 4

Ion Exchange Treatment

Resins containing the iminodiacetic acid group will exchange for cationic mercury selectively over calcium and magnesium, but copper and cobalt are also readily exchanged. Mercury in the form of anionic complexes, such as HgCl_3^- , can be treated by anion exchange resins. The thiol resin, Duolite GT-73, is reported to be selective for mercury in any of its three oxidation states (Ritter and Bibler, 1992).

Ion exchange processes are typically operated as packed columns. Usually four operations are carried out in a complete ion exchange cycle: service, backwash, regeneration, and rinse. In the service step, the ion exchange resin in the packed column is contacted with the water containing the mercury to be removed. After a target concentration of mercury in the column effluent is reached, the resin is said to be spent. A backwash step is then initiated to expand the bed and to remove fines that may be clogging the packed bed. The spent resin is then regenerated by exposing it to a concentrated solution of the original exchange ion, so that a reverse exchange process occurs. The rinse step removes excess regeneration solution before the column is brought back online for the next service cycle.

Reported advantages and disadvantages of ion exchange include (Clifford et al., 1986):

Advantages

- Operates on demand
- Is relatively insensitive to variability
- Can achieve essentially a zero level of effluent contaminant
- Is available in a large variety of specific resins
- Can normally achieve beneficial selectivity reversal upon regeneration

Disadvantages

- Has potential for chromatographic effluent peaking
- Results in spent regenerant brine that must be disposed of
- Can yield variable effluent quality

- Cannot typically be used for waters with a high total dissolved solids content

Ion exchange technology for mercury removal has historically been limited to the use of anion resins to treat industrial wastewater that contains inorganic mercury in the complex mercuric chloride form. For the process to be effective, the chloride content of the wastewater must be high, such as that generated by a chlor-alkali plant. This will yield negatively charged mercury chloride complexes. If the chloride content of the wastewater is low, either chlorine or chloride salt could be added to improve removal process efficiency (Sorg, 1979).

Cation exchange of mercury may be effective if the anion content of the wastewater is low (Sorg, 1979). Certain cation exchange resins (Amberlite IR-120 and Dowex-50W-X8) are reported to be effective for ion exchange treatment of mercury present in industrial wastewater (Patterson, 1985). Also, Duolite GT-73, a cationic resin, contains the thiol (-SH) group and reacts with ionic mercury. The thiol functional group has a high selectivity for mercury as well as a strong tendency to bind certain other metal ions such as copper, silver, cadmium, and lead.

A chelate resin is an insoluble polymer to which is attached a complexing group or groups. This, in turn, can bond metal cations within the structure so as to form a ring (or chelate) into which the metal is incorporated. The reaction involves both ion-exchange and chemical reactions. Table 4-1 lists some chelate resins that are reported to have a high selectivity for mercury; the table includes the order of selectivity.

Example ion exchange treatment data for drinking water are presented in Table 4-2. Mercury removal from ground water was studied in point-of-entry treatment (POET) systems installed on private water supply wells (Sites and Obholtzer, 1992). Table 4-2 indicates that Ionac SR-4, Purolite S-920, AFP-329, and ASB-2 were able to remove mercury from the relatively low initial ground-water concentrations to below $1 \mu\text{g/L}$, following prefiltration.

A full-scale ion exchange process at a defense processes facility has consistently removed mercury via ion exchange from 0.2 to 70 mg/L down to levels of 1 to 5 $\mu\text{g/L}$, following 0.2 μm prefiltration (Ritter and Bibler, 1992). This system utilizes a macroporous, weakly acidic, polystyrene/divinylbenzene cation resin, with thiol (SH) functional groups. High levels of mercury in a synthetic wastewater

Table 4-1. Summary of mercury-selective chelate resins (After Calmon, 1981)

Resin	Order of Selectivity
Duolite ES-466	$\text{Hg}^{2+} > \text{Cu}^{2+} > \text{Fe}^{2+} > \text{Ni}^{2+} > \text{Pb}^{2+} > \text{Mn}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+$
Dowex A-I	$\text{Cu}^{2+} > \text{Hg}^{2+} > \text{Ni}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{Cd}^{2+} > \text{Fe}^{2+} > \text{Mn}^{2+} > \text{Ca}^{2+} > \text{Na}^+$
Nisso Alm-525	$\text{Hg}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Ag}^+ > \text{Cr}^{3+} > \text{Ni}^{2+}$
Diaion CR-I 0	$\text{Hg}^{2+} > \text{Cu}^{2+} > \text{Pb}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Ba}^{2+} > \text{Sr}^{2+} > > > \text{Na}^+$
Amberlite IRC-718	$\text{Hg}^{2+} > \text{Cu}^{2+} > \text{Pb}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Co}^{2+} > \text{Fe}^{2+} > \text{Mn}^{2+} > \text{Ca}^{2+}$
Unicellex UR-10	$\text{Hg}^{2+} > \text{Cu}^{2+} > \text{Fe}^{3+} > \text{Al}^{3+} > \text{Fe}^{2+} > \text{Ni}^{2+} > \text{Pb}^{2+} > \text{Cr}^{3+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Ag}^{2+} > \text{Mn}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+} > > > \text{Na}^+$
Sirorez-Cu	pH>5, Cu^{2+} ; pH>0, Hg^{2+}
Sumichelate Q-I 0	$\text{HgCl}_2 > \text{AuCl}_4^- > \text{Ag}^+ > \text{Cr}_2\text{O}_7^{2-}$

Table 4-2. ion Exchange treatment for mercury in drinking water

ion Exchange Resin	Resin Type	Mercury Concentration ($\mu\text{g/L}$)		Additional Treatment	Other Conditions	Reference
		Initial	Final			
Ionac SR-4	Weak acid chelating resin	14.88"	0.43"	Prefiltration	GW, FS ^b	Sites and Oveholtzer, 1992
Purolite s-920	Hg-specific chelating resin	10.67"	0.34"	Prefiltration	GW, FS ^b	Sites and Obeholtzer, 1992
AFP-329	Weak base anion resin	12.21"	0.44 ^a	Prefiltration	GW, FS ^b	Sites and Oveholtzer, 1992
ASB-2	Strong base anion resin	14.31"	0.70"	Prefiltration	GW, FS ^b	Sites and Oveholtzer, 1992
Duolite GT-73	Weak acid cation thiol	200-70,000	1-5	0.2 μm prefilter	DFW, FS	Ritter and Bibler, 1992
Amberlite IRC 718	Iminodiacetic acid resin	11,800	15-35	None	SW, BS	Becker and Eldrich, 1993
IRC 718 and GT 73	(See above)	14,000	15-l ,200	GT 73 used as polishing	SMW, BS	Becker and Eldrich, 1993

^aAverage value
^b3 to 4 gpm

GW = Ground water.
 FS = Full scale.
 DFW = Defense facility wastewater.
 SW = Synthetic wastewater.
 BS = Bench scale.
 SMW = Smelter wastewater.

were removed to levels as low as 15 $\mu\text{g/L}$ after 77 bed volumes of usage, and 35 $\mu\text{g/L}$ after 157 bed volumes of usage (Becker and Eldrich, 1993). This system utilized Amberlite IRC 718 in bench-scale testing. In further bench-scale testing, smelter wastewater containing 14.0 mg/L of mercury at a flow rate of 6.7 mL/min was treated with IRC 718 followed by a polishing ion exchange column containing GT 73. This system removed mercury to concentrations of 15 to 46 $\mu\text{g/L}$ after 289 bed volumes, and 1,200 $\mu\text{g/L}$ after 325 bed volumes. This

study further showed that at pH 1.5, the iminodiacetic acid resin (IRC 718) was highly selective for mercury (II) over zinc, lead, and cadmium, and that mercury recovery from wastewater on such a resin is feasible provided strongly complexing anions such as chloride are absent. Regeneration with 3 M NaCl or other complexant for mercury at near neutral pH yields a solution for which mercury can reportedly be recovered via reduction to an insoluble and commercially valuable form (Becker and Eldrich, 1993).

Chapter 5

Other Processes

In addition to precipitation, adsorption, and ion exchange treatment technologies, the following processes are also reported to be applicable to remove mercury from wastewater: (1) chemical reduction, (2) membrane separation, and (3) various emerging technologies.

5.1 Chemical Reduction

The standard electrode potential of metals determines their placement in the electromotive series, which is a series of elements in descending order of their standard potential. Ionic mercury can be displaced from solution via reduction by another metal higher in the electromotive series, and then separated by filtration or other solids separation technique. Reducing agents include aluminum, zinc, iron, hydrazine, stannous chloride, and sodium borohydride. Example data on these reductants are presented in Table 5-1.

Although the literature includes much discussion of reduction processes, only limited actual treatment data are presented. The main advantage claimed for reduction is that mercury can be recovered in the metallic state (Patterson, 1985). The data in Table 5-1, however, indicate that most reduction processes cannot effectively achieve mercury levels below 100 $\mu\text{g/L}$, and their use would likely require second-stage polishing.

Experiments were conducted by Gould and colleagues (1984) at bench scale on Chemical Oxygen Demand (COD) test wastewater using iron wire (nominal diameter 0.229 mm). Due to the high initial mercury levels (735 to 2,030 mg/L), high recovery efficiencies were observed (96% to 99%); however, high residual mercury levels were also observed (22 to 33 mg/L). Experiments were conducted by Grau and Bisang (1995) on synthetic wastewater with iron felt formed by compressing iron wool. As for other studies, a high removal efficiency resulted at the high initial mercury concentration, leaving 68 to 91 $\mu\text{g/L}$ residual mercury.

As noted in Chapter 4, 'mercury removal from ground water was studied in POET systems that were installed on private water supply wells (Sites and Oberholtzer, 1992). Table 5-1 shows that a bimetallic oxidation/reduction compound, KDF, which consists of a finely ground alloy of 55% copper and 45% zinc, was able to remove low levels of mercury down to a range of 0.4 to 1.08 $\mu\text{g/L}$, following prefiltration. This process may be applicable only for exceptionally clean solutions, however.

5.2 Membrane Separation

Several membrane processes have been applied for water and wastewater mercury treatment. These include ultrafiltration, charged filtration, crossflow microfiltration, magnetic filtration, and reverse osmosis. Example treatment data for these processes are shown in Table 5-2.

Ultrafiltration systems are pressure-driven membrane operations that use porous membranes for the removal of dissolved and colloidal material (Metcalf and Eddy, 1991). These systems differ from reverse osmosis systems by the relative driving pressures, usually under 150 psi (1034 kN/m²). Ultrafiltration is normally used to remove colloidal material and large molecules with molecular weights in excess of 5,000. Recent studies indicate that effluent from ultrafiltration using spiral wound elements is suitable as a feed source for reverse osmosis (Metcalf and Eddy, 1991).

Chelation in combination with ultrafiltration is a process that has been described for the removal of heavy metals, including mercury (Kosarek, 1981). This concept is based on reacting ligands with cationic metallic constituents to form a metal-containing complex (chelate), and then removing these metal-containing complexes by ultrafiltration (Kosarek, 1981). The opposite charges of the ionized ligand and metal attract each other to form a stable chelate complex. The properties that facilitate ultrafiltration membrane rejection of the metal-containing complex (including mercury complexes) are thought to be (1) the increased size of the metal chelate complexes, (2) alteration in the ionic shape of the metal, (3) modified solubility, and (4) reversal of charge from cationic metal to a functionally anionic or electroneutral chelate species (Kosarek, 1981).

Charged membrane ultrafiltration incorporates a noncellulosic, high flux membrane that is negatively charged as a result of dissociated subgroups within the membrane structure. A beneficial aspect of the charged ultrafiltration membrane is that the negative polarization minimizes membrane fouling (Kosarek, 1981). Bhat-tacharyya and colleagues (1979) conducted bench-scale investigations to determine the feasibility of the simultaneous separation of various heavy metals from scrubber blowdown wastewater generated in the primary copper industry. They studied the application of low pressure ultrafiltration with commercially available, negatively charged noncellulosic membranes. Typical mercury values

Table 5-1. Performance of Reduction Processes for Mercury Treatment.

Reductant	Mercury ($\mu\text{g/L}$)		Treatment pH	Reference
	Initial	Final		
Zinc	5,000-10,000	5-10	NA	Patterson, 1985
	1,800	140	11.5	Patterson, 1985
	12,500	830	10.0	Patterson, 1985
	12,500	750	6.0	Patterson, 1985
	12,500	470	2.5	Patterson, 1985
	NA	600	NA	Patterson, 1985
Iron	734,000- 2,030,000	22,000 -33,000	NA	Gould et al., 1984
Iron felt	100,000	68-91	NA	Grau and Bisang, 1995
KDF ^a	6.17-12.11	0.4-1.08	NA	Sites and Oberholtzer, 1992
Stannous chloride	2,800	500	NA	Patterson, 1985
Sodium borohydride	10,000	220	NA	Patterson, 1985
	4,000	420	NA	Patterson, 1985
	26,000	820	NA	Patterson, 1985
	4,700	200	NA	Patterson, 1985
	NA	<10	NA	Patterson, 1985

^aBimetallic copper-zinc oxidation/reduction compound.

NA = Not available.

in the scrubber blowdown were found to be 1.5 to 2.0 mg/L. Mercury removals for a full-scale system were calculated by computer simulation based on laboratory-scale data and were reported to be 91% to 93% ($AP = 5.6 \times 10^5 \text{ N/m}^2$, channel velocity, $U = 250 \text{ cm/s}$, and $\text{pH} = 4.5$). For a $3.6 \times 10^5 \text{ kg/d}$ (400 ton /day) copper production plant, the net operating costs for a closed-loop scrubber blowdown water recycle system was estimated to be \$2,508 /day or \$0.0070/kg Cu production (1995 basis updated assuming cost components follow change in skilled labor cost index).

The crossflow microfiltration system is based on the concept of using a dynamic membrane to form a filtration medium. This process, whose patented form is called Exxflow, is a solid-liquid separation process in which the feed suspension sweeps across the face of a filter membrane while pressure differences cause the liquid phase to pass through the membrane, leaving the solids to be flushed away in the residual flow. By this means, the solids are concentrated up in the suspension flow, which is commonly recycled to the feed end. This contrasts with "barrier" filtration systems in which the solids build up on the filtering surface, gradually restricting the flow through

the filter (Squires, 1992). A schematic of the microfiltration process is shown in Figure 5-1.

Mercury removal via crossflow microfiltration was reported for a full-scale plant designed to process 200 m^3 /day of mixed plating wastewater (Broom et al., 1994). A process schematic of the plant is shown in Figure 5-2. The filtrate from the rotary vacuum filter was combined with the supernatant from a preclarification stage and stored in a 80 m^3 balance tank, where the pH was adjusted to 11 to 12, primarily to precipitate cadmium. Sodium hydrogen sulfide (NaHS) was also added to precipitate any soluble metals remaining. This conditioned filtrate was then pumped to the crossflow microfiltration unit, where it was recycled at an average pressure of 150 kPa. The reject flow was effectively a concentrate produced by the passage of clean permeate through the filter. With mercury feed concentrations to the microfiltration plant of 1.27, 0.967, 0.15, and 2.28 mg/L, permeate concentrations of 0.015, 0.015, 0.088, and 0.03 mg/L were achieved, respectively. This represents a removal efficiency of about 95 %. Removal may have been enhanced by mercury co-precipitation in the balance tank.

Table 5-2. Performance of Membrane Processes for Mercury Treatment.

Membrane Process	Mercury ($\mu\text{g/L}$)		Percent Removal	Comments	Reference
	Initial	Final			
Reverse osmosis	5,000	880'	82.4	BS, SW	Sorg, 1979
	9,000	1,503'	83.3	BS, SW	
	8	1.5 ^a -1.7 ^a	79-81	PS	
Charged ultrafiltration	1,500-2,000	NA	91-93	CS	Bhattacharyya et al., 1978
Crossflow micro-filtration	1,270	15	99.8'	FS, PW	Broom et al., 1994
	967	15	98.5'	FS, PW	
	150	88	41.3'	FS, PW	
	2,280	30	98.7"	FS, PW	
Magnetic filtration	15,000	3-117	99.2-99.9	BS, GSW	Terashima et al., 1986

^aCalculated from removal efficiency data (% removal = $\frac{\text{Initial} - \text{Final}}{\text{Initial}} \times 100\%$)

BS = Bench scale.
 SW = Spiked wastewater (secondary effluent).
 PS = Pilot scale.
 cs = Computer simulation.
 FS = Full scale.
 PW = Plating wastewater.
 GSW = Gas scrubber wastewater from solid waste incineration plant.
 NA = Not available.

Magnetic filtration of soluble species such as ionic metal is accomplished by forming a magnetic precipitate through coagulation and magnetic seed addition, and then passing the wastewater through a filter made with ferromagnetic wires, which represent a magnetic field. The magnetic precipitate can be rapidly and efficiently removed by magnetic filtration, even if the precipitate is quite fine (Terashima et al., 1986). This occurs because of the strong magnetic forces that act on the magnetic particles as they move through the magnetic field. The magnetic particles are captured on the filter matrix by the magnetic force, which overcomes other competing forces of gravitation, hydrodynamics, and inertia (Terashima et al., 1986). Terashima and colleagues (1986) report mercury removals in a bench-scale magnetic-filtration unit fed gas scrubbing wastewater from a municipal solid waste incineration plant. For an influent mercury concentration of 15.0 mg/L, effluent mercury concentrations of 0.003 to 0.117 mg/L were achieved.

Reverse osmosis (RO) is a physical separation technique whereby an applied pressure in excess of the inherent solution osmotic pressure forces water to permeate a semipermeable membrane, which rejects the bulk of the dissolved and suspended constituents. The pressures applied to the membrane in RO processes range from 200 to 800 psi (Kosarek, 1981). The operation of an RO

membrane system is significantly affected by fouling, scaling, pH-temperature-pressure-related hydrolysis, and chemical or biochemical deterioration of the membranes. The RO process has very strict feed water requirements, particularly related to the concentration of suspended solids and materials (e.g., oil or grease), which will foul the membrane surface (Kosarek, 1981).

A literature review by Sorg (1979) described several laboratory and pilot-plant RO studies for the removal of metals from water or wastewater, but only one study provided data on the removal of mercury. Investigators ran a series of RO pilot-plant tests to evaluate the technique for the removal of heavy metals, pesticides, and other toxic chemicals from secondary waste water effluent. The results of one-day batch tests with spiked concentrations of 5 and 9 mg/L of inorganic mercury showed removals of 82.4% and 83.3%, respectively.

Sorg (1979) also reported that EPA's Drinking Water Research Division (DWRD) conducted two one-day tests for inorganic mercury (influent at 0.008 mg/L) removal from Glendale, Ohio, well water, with two small-scale RO systems. The first system used a spiral-wound (SW) membrane and the second a hollow fiber (HF) membrane. The SW system had a raw water flow of 2.2 Lpm and operated at 1,400 to 1,600 kPa (200 to 230 psi) and 7% to 9% recovery. The HF system had a higher raw water flow

Table 7-1. Nonradioactive Contaminants and Discharge Limits (After Bibler and Wallace, 1987).

Ion	Influent to ETF (ppm)		Influent to Ion Exchange (ppm)		Proposed Limits (ppm)	
	Average	Maximum	Average	Maximum	Average	Maximum
NH ₄ ⁺	16	110	4.0×10^{-1}	2.8	20	—
Hg ²⁺	0.053	10	1.3×10^{-2}	2.4×10^{-1}	4.5×10^{-1}	1.75×10^{-1}
Zn ²⁺	1.1	100	2.8×10^{-2}	2.5	1.48	2.61
Cr ³	0.031	240	7.8×10^{-4}	6.0	1.71	2.77
Cu ²⁺	0.14	18	3.5×10^{-3}	5.0×10^{-1}	1.30	1.89
Pb ²⁺	0.15	38	3.8×10^{-3}	9.5×10^{-1}	2.2×10^{-1}	4.5×10^{-1}
Mn ²⁺	0.18	21	4.5×10^{-3}	5.3×10^{-1}	—	—
NO ₃ ⁻	1,015	22,400	25	560	—	—

Table 7-2. Radioactive Contaminants and Discharge Limits (After Bibler and Wallace, 1987).

Radionuclide	Influent to Ion Exchange		Release to Streams		DOE Guide
	mCi/yr	mCi/mL	mCi/yr	mCi/mL	mCi/mL
cs- 134,137	70	1.7×10^{-10}	0.7	1.7×10^{-12}	2.9×10^{-5}
Sr - 89, 90	9	2.2×10^{-11}	0.09	2.2×10^{-13}	3.3×10^{-6}
Co-60	5	1.2×10^{-10}	0.5	1.2×10^{-12}	3.0×10^{-5}
Other p-y	3.0	7.5×10^{-12}	3.0	7.5×10^{-12}	—
Total a	3.5×10^{-2}	8.7×10^{-3}	3.5×10^{-3}	8.7×10^{-15}	—

indicating that simple storage was a viable option. Similar resin samples were incorporated in Portland Type II grout and subjected to structural integrity tests and the Extraction Procedure (EP) toxicity test. These samples passed the structural integrity test but not the EP toxicity test. Because the EP toxicity test involved maintaining the sample at pH 5 with acetic acid and given the high concentration of calcium ions in grout, exchange of calcium ions for mercuric ions may have taken place. Thus, the storage of spent resin without incorporation into grout was preferred.

Although regeneration of the spent resin is possible, it is not deemed desirable at ETF. Mercury can be eluted from the resin using 3 M HCl or 2 M NaSCN, neither of which is chemically compatible with materials of construction or processes at SRS. Dissolution of the resin and reclamation of mercury by chemical means such as precipitation as the sulfide or reduction to the metal is an

attractive alternative to storage, should recovery and removal become desirable.

Sulfonic Acid Cation Resins

A macroporous, strong acid cation exchange resin was chosen for removal of cesium and strontium. Several commercially available resins have demonstrated cesium and strontium removal capabilities coupled with ease of regeneration. Cesium and strontium in the regenerant can be by a relatively small volume of neutral reagent be concentrated further and incorporated in concrete for final disposal. Spent resin can be decontaminated and discarded in an approved manner.

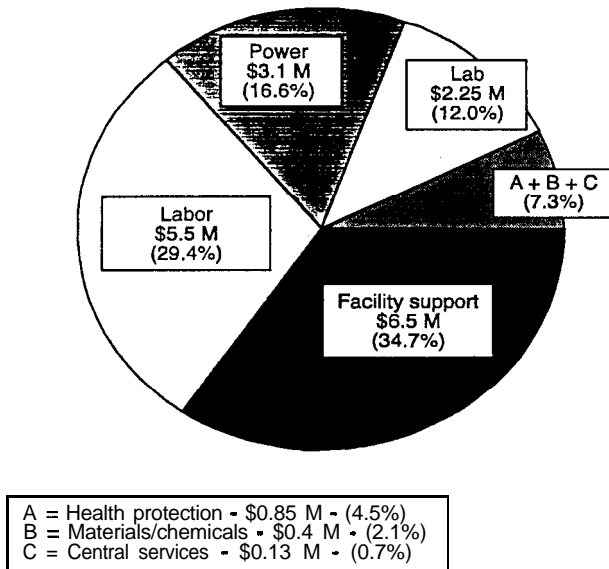
Several test runs were conducted to determine the performance of the sulfonic acid resin throughout several simulated feed, wash, and regeneration cycles. Results indicated that the effectiveness of the process was less

than desirable after several cycles had been completed. A chromatographic effect was observed where concentrated bands of all metals present were detected in the effluent at unpredictable times during feed cycles. The frequency and concentrations of such eluted bands cannot be accurately predicted in the ETF due to the varying daily concentrations of influent to the facility. To prevent this behavior the ion exchange feed was first processed through the Duolite GT-73 columns for mercury removal, allowing the sulfonic acid columns to operate as designed for the removal of cesium and strontium.

7.2 Effluent Treatment Facility Economics

The treatment plant operates Friday through Sunday of each week. There are 5 operators during each shift, which lasts 12 hours, with an additional 0.5 hour turnaround. During the 1994 fiscal year, 22 million gallons of waste water were treated at a total cost of \$18.8 million. This results in a unit cost of about \$1/gallon. Figure 8-2 presents the ETF cost breakdown components.

Figure 7-2. ETF facility O&M cost breakdown.



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